

Center: Consortium for Materials Development in Space
The University of Alabama in Huntsville (UAH)

Project Name: "Highly Non-Linear Optical Organic Crystals and Films"

Subproject Name: "Highly Non-Linear Optical (NLO) Organic Crystals"

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Introduction

This project involves the synthesis and characterization of organic materials having powerful nonlinear optical (NLO) properties and the growth of highly ordered crystals and monomolecular films of these materials. As such we are conducting research in four areas: (1) theoretical design of new materials; (2) characterization of NLO materials; (3) synthesis of new materials and development of coupling procedures for forming layered films; and (4) improvement of the techniques for vapor-phase and solution-phase growth of high-quality organic crystals. This knowledge will form the basis for experiments on growth of these crystals in microgravity.

Recent Activities

Work over the past year has proceeded in all four of the above areas: First, we have continued work with a new apparatus for better defining parameters required to grow crystals of NLO materials by vapor deposition. Second, we have continued development of the chemistry required to prepare new NLO materials and couple them to surfaces. And third, studies into characterizing and

predicting NLO properties have continued. In addition IBM has agreed to cooperate with the Consortium as our partner on this project.

1. Crystal Growth

We have in hand an apparatus for vapor phase crystal growth that will be flown on the Shuttle. This simple apparatus consists of a 4 inch by 0.75 inch glass tube, divided in the middle by an O-ring joint. One half of the tube is the hot end, while the other is the cold end. To provide precise temperature control ($\pm 0.05^{\circ}\text{C}$), the hot and cold ends have separate wrappings of resistance wire. A stopcock near the center provides access to vacuum. A low energy loss apparatus has been designed by Fran Wessling for incorporation of the tubes into the GAS can. See the appendix for a description of the device.

This apparatus has been used to examine the effects of temperature and pressure on size of crystals from methylnitroaniline (MNA). It has become clear that the best crystals are obtained by slow (2-3 days) crystal growth with small ($2-5^{\circ}\text{C}$) temperature gaps between hot and cold ends.

We have recently begun collaboration with F. Rosenberger on better defining conditions for crystal growth and on interpreting the results. As a result of this collaboration and our previous experience we have constructed a new apparatus to better control crystal growth. This apparatus has two new features. First, rather than having a cold end, the new device has a cold "sting" made of gold. This permits maintaining the temperature of the entire tube at the "hot" temperature, with the exception of the sting which has its own separate temperature control. With this alteration we should avoid growth of crystals along the walls of the tube. Secondly, the new tube has controlled flow of inert gas down the tube. With this alteration we can control diffusion rates of vapor down the

tube. Diffusion rates of the organic material will be measured at various positions in the tube by light scattering.

This apparatus is being used to better define crystal growth conditions for our first shuttle flight with the simple apparatus (described first above). Also, it is our goal to fly a much more sophisticated apparatus such as the Rosenberger device on subsequent Shuttle flights.

As a second part of this work, we have now begun growing crystals of the betaines by solution crystal growth. Preliminary studies appear promising as some crystals have already been prepared. These materials will be used for structure determination by x-ray crystallography and for measurement of the second order nonlinearity ($\chi^{(2)}$) by frequency doubling.

2. Synthesis of NLO Materials and Coupling Chemistry

A major interest here is in synthesis and characterization of betaine dyes as NLO materials. The synthetic approaches were described in the previous annual report. We have now shown that these approaches work, and we have prepared four new betaines. The second-order nonlinearity values (β) for these compounds will be determined by means of the solvatochromic method. All the materials are highly solvatochromatic, and thus from preliminary examination appear to be highly interesting. From this work should come a better understanding of the molecular properties leading to solvatochromism and NLO properties. Additionally, we are in the process of preparing a fifth betaine derivative incorporating an optically active center to ensure crystallization in an enantiomorphous space group.

A second task in this area is to couple betaines to surfaces as monolayers and multilayers. The carboxyl derivative has been synthesized for this purpose